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Semiconductor ceramics for NTC thermistors: the reliability aspects

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Abstract

Thermally induced processes in ceramic–electrode interfaces of $Cu_xNi_{1-x-y}Co_{2y}Mn_{2-y}O_4$-based NTC thermistors as a function of their chemical compositions and quantitative parameters of low-temperature annealing at 400–800° C are studied. Thermal treatment of thermistors at 400-600° C during 15 h leads to degradation of the metallization layers for the majority of the investigated samples owing to the migration of electrode material (silver) into ceramic body. An accompanying anomalous increase of thermistors' electrical conductivity is observed. The following thermal treatment during 15 h at 800°C leads to an electrical conductivity regeneration to, approximately, the initial values. The reversible nature of this phenomenon is confirmed by Auger-spectroscopy method. Some of the studied NTC thermistors appear to be stable to low-temperature thermal treatment. These compositions are proposed for applications in devices operating at the temperatures up to 530° C.

Keywords: Electrical conductivity; Electron microscopy; Spinels; Thermistors

1. Introduction

Negative temperature coefficient (NTC) thermistors based on spinel-structured semiconductor ceramics (SSSC) are widely used for temperature measurement and compensation, inrush current limiting, etc.[1–3] To satisfy the above device applications, the SSSC must be stable and possess a set of necessary electrical characteristics.

There are different sources of NTC thermistors instability. They include, among others, the changes in SSSC chemical composition, the cation rearrangements in crystal structure and the interactions in ceramic–electrode interface.[4–6] The reliability of these electronic components, as it was shown previously,[4] is mainly determined by the nature of the metallic electrodes and technological features of its formation.

Silver paste, fired on flat surfaces of ceramic blanks sintered at high temperatures (up to 900–1300°C), is usually used for thermistors metallization. It is known that silver becomes useless for NTC thermistors operating at higher temperatures (>300°C) because of significant metal migration processes in the ceramic body, as well as in the encapsulating materials.[7]

The analogous mass-transfer processes at the border between the ceramic body and silver electrode under the influence of so-called low-temperature (400–800°C) thermal annealing were investigated in previous work.[8] However, the quantitative parameters of these processes were obtained only for $Cu_{0.2}Ni_{0.4}Co_{0.8}Mn_{1.6}O_4$-based samples.

The aim of this work is to study the thermally induced processes in ceramic–electrode interfaces for samples representing the whole $Cu_xNi_{1-x-y}Co_{2y}Mn_{2-y}O_4$ chemical system as a function of their chemical compositions and parameters of low-temperature annealing (thermal treatment at 400–800°C).

2. Experimental

Fourteen different SSSC compositions in the $Cu_x Ni_{1-x-y}Co_{2y}Mn_{2-y}O_4$ ($0.1 \leqslant x \leqslant 0.8$; $0.1 \leqslant y \leqslant 0.9–x$) system (Table 1) were chosen for experiments. The traditional ceramics processing technology was applied.[1]

High purity and tested raw materials (copper, nickel, cobalt and manganese carbonates) were used as initial

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Table 1
Chemical composition of $Cu_xNi_{1-x-y}Co_{2y}Mn_{2-y}O_4$-based ceramics

Composition no. →	1	2	3	4	5	6	7	8	9	10	11	12	13	14
x	0.1	0.2	0.45	0.8	0.45	0.1	0.1	0.2	0.4	0.6	0.4	0.2	0.2	0.33
y	0.8	0.7	0.45	0.1	0.1	0.1	0.45	0.6	0.4	0.2	0.2	0.2	0.4	0.34

components for SSSC synthesis. The precise combinations of salts were prepared and wet mixed. The thermal decomposition of the obtained mixtures was performed in air at 700±5°C for 5 h. The obtained powders were milled, blended with an organic binder and pressed into disks (d=7.8–11.5 mm). The blanks, prepared in such way, were sintered in air at 900–1300°C depending on their chemical compositions. The sintering temperature is indicated in the lower index of the sample designation: the "1" index corresponds to 900, the "2" to 1000, the "3" to 1100, the "4" to 1200 and the "5" to 1300°C. The blanks without metallic electrodes are referred to as type I samples.

To obtain type II samples (with silver electrodes) the silver paste was fired onto the flat surfaces of the SSSC disks at 830±5°C (metallization treatment).

The low-temperature annealing was performed in air for type I samples, sintered at 800°C and then fast cooled, and type II samples, after metallization treatment. The investigated NTC thermistors were monotonously heated (25°C/min) up to a certain temperature in the range of 400–800°C, kept at this temperature for 15 h, and then drastically cooled to room temperature (for 2–3 min). The sequences of the low-temperature thermal treatments in different regimes (A_1, A_2 and A_3) are presented in Fig. 1.

The electrical measurements were carried out on type II samples in the normal conditions (25°C) by the four-wire line compensation method. The quantitative chemical compositions of the samples were checked by electron-probe microanalysis using the Camebax device (K_α line for Cu, Ni, Co, Mn and L_α for Ag). The profile concentrations of the deep distribution of elements with 10^{-4} μm resolution and spatial resolution of 50 nm were obtained by Auger spectroscopy (scanning electron microscope Jamp-10S).

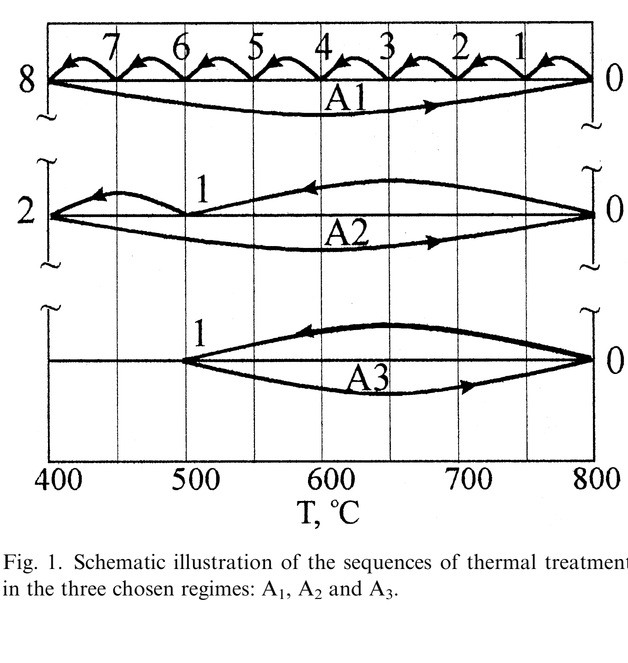

Fig. 1. Schematic illustration of the sequences of thermal treatments in the three chosen regimes: A_1, A_2 and A_3.

3. Results and discussion

The electrical conductivity at 25°C (σ_{25}) of type II samples, annealed at eight different temperatures from 800 to 400°C with 50°C steps according to A_1 regime, strongly depends on the temperature of this additional treatment (Fig. 2). For the majority of the investigated samples the values of σ_{25} considerably increase with the temperature decreasing from 800 to approximately

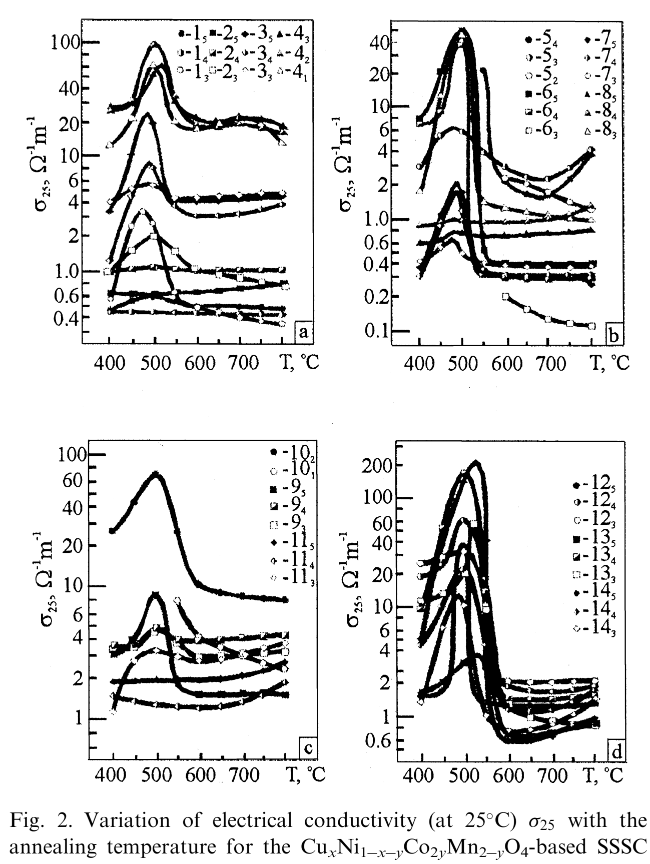

Fig. 2. Variation of electrical conductivity (at 25°C) σ_{25} with the annealing temperature for the $Cu_xNi_{1-x-y}Co_{2y}Mn_{2-y}O_4$-based SSSC samples.

550°C (0→5 annealing steps, Fig. 1), then $\sigma_{25}(T)$ dependences achieve the anomalous maxima at the certain characteristic temperature T_c at 500–550°C and decrease with the following temperature drop from 500 to 400°C (6→8 steps, Fig. 1).

To answer the question if the observed thermally induced changes of the σ_{25} at the temperatures near T_c were partially influenced by the previous annealing steps, the additional thermal treatments according to A_2 regime were carried out. Within the limits of measurement faults, the σ_{25} values, obtained as the result of different regimes (A_1 and A_2) of thermal treatments, coincide. This means that, finally, the changes of the electrical conductivity, being independent on the sequence of thermal treatments, are determined only by the annealing temperature.

The kinetic study of these thermally induced changes for the $4_{1,2,3}$ and $12_{3,4,5}$ type II samples, annealed at the characteristic temperatures T_c, shows that R_{25} decreases during approximately 13 h and then saturates (Fig. 3). This is why the chosen duration of thermal treatments was 15 h.

As one can see from Fig. 2, the changes of electrical conductivity for type II SSSC samples under the influence of low-temperature annealing at 400–800°C are sufficiently different. It is impossible to obtain the dependences of electrical conductivity at 400–600°C for $5_{2,4}$, 6_3 and 10_1 samples owing to intensive degradation of their metallizing layers, caused by thermally induced processes in ceramic–electrode interfaces (Fig. 2). The silver electrodes disappear at these temperatures (this can be observed visually) due to metal migration into the ceramic body. Similar effects were observed by other authors.[7] In contrast, the 1_4, 2_4, $8_{4,5}$ and $11_{3,4,5}$ samples either show a weak monotonous σ_{25} decrease with annealing temperature or appear to be completely independent of thermal treatment. These SSSC samples can be proposed as perspective materials for devices operating at temperatures up to 530°C.

The observed thermally induced changes of the σ_{25} are reversible. The following annealing at 800°C (for 15 h) according to A_1 regime (8→0 annealing step, Fig. 1) leads to an electrical conductivity regeneration to, approximately, the initial values. Furthermore, the σ_{25} values for the $5_{2,4}$, 6_3 and 10_1 samples which completely destroyed metallic electrodes at 400–600°C, can be measured owing to their renewal. The reversible variations of the electrical conductivity for type II samples of compositions 1, 4 and 12, induced by periodical thermal treatments at 800 and 500°C (according to A_3 regime, Fig. 1) are shown in Fig. 4.

The Auger spectroscopy and electron-sonde microanalysis methods were used to explain the nature of the observed effects in the SSSC samples. The micrographs of the shearing of 13_4 samples of the both types (type I and II), annealed at 525 and 800°C, were presented in a previous paper.[8] These investigations allow us to conclude that the decomposition of ceramic material under the influence of annealing at 525°C and the metallic silver (from silver electrodes) migration through the sections of thermally destroyed crystallite boundaries into the ceramic body are present.

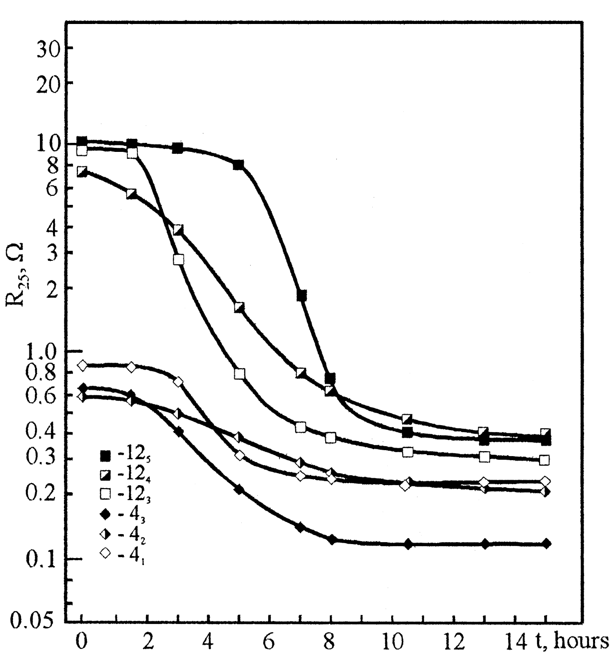

Fig. 3. Variation of the electrical resistance (at 25°C) R_{25} as a function of thermal annealing duration at T_c for the type II $4_{1,2,3}$ and $12_{3,4,5}$ SSSC samples.

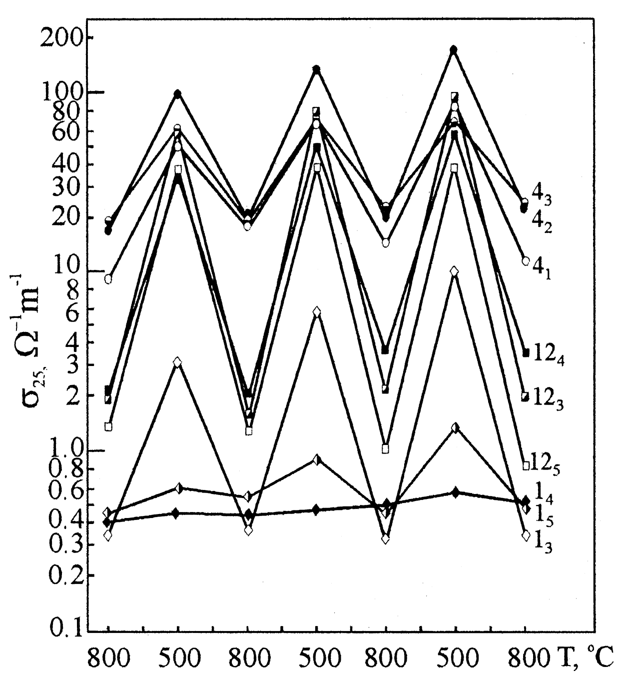

Fig. 4. Variation of electrical conductivity σ_{25} for the type II samples of 1, 4 and 12 compositions in the $Cu_xNi_{1-x-y}Co_{2y}Mn_{2-y}O_4$ system with multiple cycles of thermal annealing according to A_3 regime.

The processes of thermally stimulated migration of silver into the ceramic body were also identified by the profile investigations of composition using Camebax electron-probe microanalyser. This study detected the presence of silver atoms only in the regions of metallic electrodes for the type II 13_4 samples, annealed at 800°C. For the same samples, annealed at 525°C, silver is revealed in the ceramic body too.

The micrographs obtained in the secondary electrons of Ag for the type II 13_4 sample shearing, after subsequent heat treatments at 800 (a), 525 (b) and 800°C (c), are shown in Fig. 5. The well-defined Ag layer (contact region) and the relatively thin transition layer (approximately 10 μm) between Ag and ceramics are revealed in the samples annealed, for the first time, at the 800°C (Fig. 5a). The depth of Ag atoms penetration into the ceramic body rise up to approximately 50–500 μm for the samples, annealed at 525°C, depending on their chemical composition (Fig. 5b). The following thermal treatment at 800°C leads to the renewal of the contact layer. The content of Ag in the ceramic body decreases considerably. As a result, only the Ag traces can be revealed in this case (Fig. 5c).

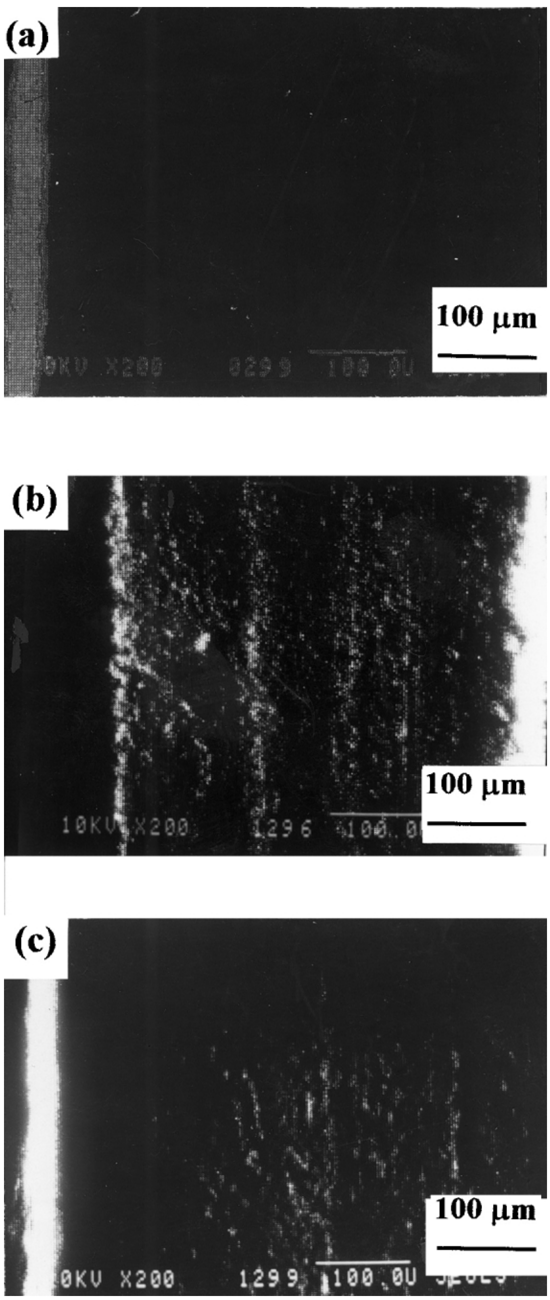

Fig. 5. Micrographs obtained in the secondary electrons of Ag for the shearing of 13_4 sample, subsequently thermally treated at 800°C (a), 525°C (b) and 800°C (c).

4. Conclusions

The influence of annealing at 400–800°C on the electrical conductivity of NTC thermistors based on $Cu_xNi_{1-x-y}Co_{2y}Mn_{2-y}O_4$ ceramics was studied. It was shown that for the majority of investigated samples, the electrical conductivity increased under the influence of thermal treatment at 400–600°C. This phenomenon was explained by degradation of the metallizing layer as the result of thermally induced migration of the contact material (silver) into ceramic body. This process was shown to be reversible. The following thermal annealing at 800°C led to the renewal of the contact layer. This conclusion was confirmed by Auger-spectroscopy method.

Some of the studied NTC thermistors were independent on the influence of thermal treatment. These ceramic semiconductors can be proposed as perspective materials for devices with increased operating temperatures (up to 530°C).

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